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Poisoning of mixed matrix membranes by fermentation components in pervaporation of ethanol

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ABSTRACT

Pervaporation is an alternative to distillation for recovering ethanol produced by fermentation of grains and biomass. Ethanol-selective mixed matrix membranes of the hydrophobic zeolite ZSM-5 in polydimethylsiloxane (PDMS) have superior performance compared to pure PDMS membranes in pervaporation of clean ethanol/water solutions, but are susceptible to performance reduction when pervaporating fermentation broths. The effects of pervaporating a variety of solutions with 60 wt% ZSM-5/PDMS membranes were studied. Corn dry-grind fermentation broth, thin stillage, and a synthetic syngas fermentation broth rapidly and significantly degraded mixed matrix membrane performance. Broths treated to remove corn oil and fatty acids were much more benign. Oleic acid, as a representative fatty acid, was identified as a significant performance reducer.

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1. Introduction

There is great interest in developing fuel ethanol derived from renewable feedstocks, and in particular, lignocellulosic feedstocks which are dedicated energy crops such as switchgrass and poplar, or wastes such as corn stover, wheat and rice straw, paper mill black liquor and municipal solid waste. A difficulty with these feedstocks is that to date lignocellulose-based fermentations are typically more dilute than high starch grain-based fermentations, and the ethanol concentration is therefore significantly lower [1–3]. Dilution is a problem when distillation is used as the alcohol recovery method, since distillation energy use (and cost) rises exponentially as distillation feed concentration drops to the 1–5 wt% ethanol range expected for lignocellulosic feedstocks [3–5]. Pervaporation has the potential to recover ethanol with a lower energy use than distillation. Pervaporation is a membrane permeation process where a feed liquid contacts the membrane on one side, and the permeate is removed as a vapor.

Commercial ethanol-selective pervaporation membranes are available. These are thin-film composite (TFC) membranes comprising several layers. A very thin active layer is required to produce commercially viable fluxes. The active layer is typically polydimethylsiloxane (PDMS) of a few microns thickness. It is mechanically supported by a microporous layer, whose surface pore size is less than the thickness of the active layer. This microporous layer in turn is supported by a non-woven fabric. The ethanol/water selectivity of PDMS, especially in thin-film composites, is poor but can be enhanced by incorporation of higher selectivity adsorbents such as a hydrophobic MFI zeolite to form a mixed-matrix membrane (MMM). Two frequently used examples of hydrophobic MFI zeolites are high silica-to-alumina ZSM-5, and silicalite-1 [6]. [7] These two zeolites are the same except silicalite-1 has no alumina in its structure, and is more hydrophobic. ZSM-5 is available at several SiO_2/Al_2O_3 ratios. Several researchers have observed a significant reduction in ethanol pervaporation performance of silicalite-1 membranes [8,9] or mixed matrix membranes incorporating silicalite-1 or ZSM-5 in PDMS [10] when pervaporation is carried out on fermentation broths as opposed to clean ethanol–water feed solutions. Acetic acid, succinic acid and glycerol have been implicated in performance reductions [10–12].

Pervaporation of fermentation broth with a TFC PDMS membrane showed stable flux and separation factor when the membrane was washed periodically [13]. Pervaporation with a TFC polyoctylmethylsiloxane (POMS) membrane, with a separation factor similar to PDMS, showed a decreased flux when glycerol or succinic acid were present, but no change in separation factor [14]. Since separation factor was not decreased, it is possible that capillary condensation of non-ethanol feed components in the fine pores of the support layer may be responsible for the decrease in flux. A vapor pressure reduction below the pure component vapor pressure value would occur, and would be more pronounced in the smaller pores, as governed by the Kelvin equation [15].

Several mechanisms may be contributing to the reduction in performance of the mixed matrix membranes. These include (1) fouling of the surface by cells or other broth components, (2) competitive adsorption in the zeolite by more strongly adsorbing

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species than ethanol, (3) absorption of components and swelling of the polymer phase, and (4) restriction of pores in the support layer of TFCs by capillary condensation for permeating species with lower volatility than ethanol. The objectives of this research are to study the influence of fermentation components on the performance of thick (not TFC) mixed matrix membranes in order to separate active layer effects from support layer effects, and to investigate membrane regeneration methods and options for pretreatment of the broth prior to membrane contact. Several approaches are taken: (1) spiking of clean ethanol–water feeds with particular components to isolate the effect of these components on membrane performance, (2) use of fermentation broths and pretreated fermentation broths, and (3) treatment of the membrane in pervaporation with the desired feed solution followed by pervaporation against a clean ethanol–water feed.

2. Experimental

2.1. Fabrication of PDMS membranes

Silicone rubber GE RTV 615 kit (General Electric, supplied by R.S. Hughes Co.) contained two liquid mixtures. Part A was a prepolymer of PDMS chains end-capped with vinyl groups, and Part B was a mixture of PDMS chains containing multiple silhydro groups and a platinum-based cross-linking catalyst. PDMS membranes were prepared by mixing RTV 615A and RTV 615B in a 10:1 ratio, degassing the mixture under vacuum, and casting on a clean glass plate using a doctor blade (Gardco "Microm" adjustable film applicator). The membranes were cured at 50 °C for 18 h.

2.2. Fabrication of ZSM-5/PDMS mixed matrix membranes

Zeolite ZSM-5 (Zeolyst International, CBV 28014) was in the ammonium form, had a SiO_2/Al_2O_3 ratio of 280, a surface area of 400 m^2/g, and an average particle size of 3.2 μm as stated by the manufacturer. A typical preparation of a nominally 60 wt% ZSM-5/PDMS membrane about 250 μm thick follows: 1.42 g ZSM-5 was weighed into a glass vial, to which was added 3.64 g isooctane (2,2,4-trimethylpentane, Sigma Aldrich, 99+%), followed by 0.87 g PDMS Part A. The mixture was shaken, then bath-sonicated for 10 min to disperse the zeolite particles. The presence of Part A during sonication was necessary for dispersion of the particles. Next, 0.087 g Part B was added and the mixture sonicated for 10 s. This mixture was poured into a rectangular Teflon mold on a leveled plate in a vacuum oven. Pressure was gradually reduced to 3 kPa over 8 min to evaporate most of the isooctane without causing formation of bubbles in the film. A slow nitrogen sweep was applied for 30 min. The sweep gas was stopped and pressure reduced to 1.4 kPa and held there for 20 min. Finally, the oven was heated to 70 °C for 5 h to cure the membrane.

To determine the dispersion of the zeolite particles in the PDMS matrix, scanning electron microscopy (SEM) images were taken of cross-sections of several of the membranes prepared by cryofracture of the ZSM-5/PDMS MMMs. The instrument used was a Hitachi S-4700 scanning electron microscope. A typical image is shown in Fig. 1. It can be seen that the 3 μm zeolite particles are uniformly distributed in the matrix, and no agglomeration is evident. While the interface between the particles and the PDMS appears to be void-free, this cannot be completely distinguished at this degree of resolution.

2.3. Equipment and operation

Prior to pervaporation, integrity of the membranes was evaluated by gas permeation. Several nitrogen permeation measurements were taken over a feed pressure range of 20–45 psig, using a bubble flowmeter to measure permeate flow. This was repeated using oxygen. Linear behavior of flow vs. pressure and a flow ratio of oxygen-to-nitrogen of 2 or better (the ratio of the two gas permeabilities for PDMS is 2.1 [16]) indicated that the membrane had no gross defects [17,18]. Membranes with lower ratios were discarded. As an indication of the sensitivity of the test, a single defect of 3.5 μm diameter would reduce the flow ratio from 2.17 to 2.00 in a 150 μm thick PDMS membrane at 40 psi differential pressure; a 10 μm defect would reduce it to 1.00.

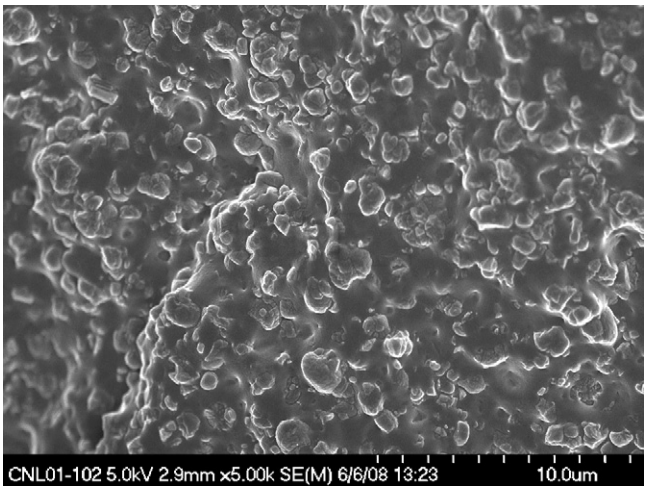

Fig. 1. SEM image of a cross-section of a 74 wt% ZSM-5/PDMS membrane prepared by cryofracture.

Three pervaporation rigs were used. One used clean ethanol–water feeds and could accommodate 3 permeation cells simultaneously (the "clean feed rig"). This was used to test membranes for baseline behavior and reasonable performance prior to entry into the experimental program. Baseline conditions were 5 wt% ethanol–water feed at 50 °C and <0.3 kPa permeate pressure. A second rig was used with broths, spiked ethanol–water solutions, or clean feeds (the "impurities rig"). Each test sequence in the impurities rig employed a new membrane. For the clean feed and impurities rigs, the feed flow was turbulent (Re = 5700 in the cell's flow channel) to avoid any issues of concentration polarization. This occurs when ethanol mass transfer through the membrane is faster than ethanol mass transfer in the feed solution, which gives rise to a boundary layer at the membrane's feed side which is depleted in ethanol.

Frequent measurements of permeate flux and concentration for a 200 μm 60 wt% ZSM-5/PDMS membrane indicated that steady state was reached by 2.5 h. Therefore, membranes were acclimated to the feeds for a 4 h period before the primary trap was opened to receive permeate. Permeate was collected over approximately 16 h, weighed and analyzed by GC. The feed solution was analyzed at the start and end of each run, and the average value used in performance calculations. Subsequent runs were carried out on the second and third day. Feed concentration was adjusted periodically due to loss of ethanol to permeation.

The third rig was for conditioning a membrane with a small amount of broth or other solution (the "conditioning rig"). Its purpose was to expose the membrane to particular feeds under pervaporation conditions, after which the membrane's performance would be measured using clean feed in the impurities rig. No performance data was taken during the conditioning period. The volume of feed was 200 ml, much less than the 4L used in the other rigs, and cleanout was substantially simpler. Membrane conditioning in this rig was done for 8 h at 50 °C and a feed flow rate of 170–300 ml/min. Permeate pressure was <0.3 kPa. The membrane

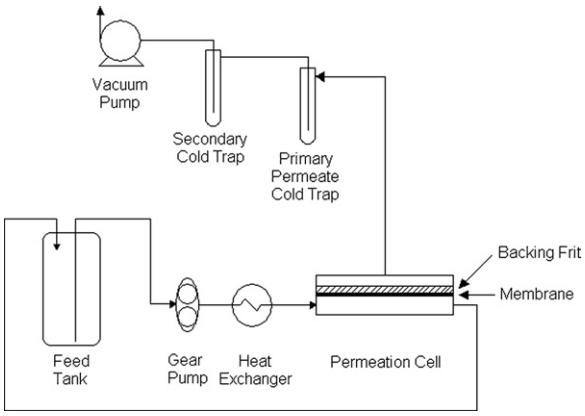

Fig. 2. Schematic of the "Clean Feed" pervaporation rig.

and cell were rinsed thoroughly with water before transfer to the impurities rig.

After pervaporation experiments were concluded, the thickness of the membrane was measured at 12 points across the surface and averaged, using a platform-style micrometer (Starrett #652JZ dial bench gage).

Each pervaporation cell was machined from stainless steel. The feed channel was rectangular, with entry and exit of the feed solution at either end, and provided 16.13 cm^2 of surface area for permeation. The membrane was held in place with EPDM o-rings, and backed on the permeate-side by a stainless steel frit.

Fig. 2 is a schematic of the clean feed rig, but for simplicity showing only one of the 3 cells and associated primary permeate traps. The feed circulation system consisted of a 316SS gear pump (Micropump model 5000/56C with PEEK gears, EPDM static seals, magnetically coupled to drive), a heat exchanger heated by a pumped hot water bath, and a 2 gallon stainless steel feed tank (Eagle Stainless). Stainless steel tubing was used throughout. Temperatures were measured by thermocouples at the outlet of each cell. The vacuum system consisted of a glass primary cold trap for each cell, a glass secondary cold trap for the entire system, and a vacuum pump (Ulvac model GLD-040). Pressure at each cell was measured by a piezo pressure transducer (0.1–1000 torr, MKS model 902) and by a Pirani gauge (1 μm–100 torr, Laco Technologies model LVG-200TC).

The impurities rig used the same permeation cell design and vacuum system design as above, but the feed system consisted of a peristaltic pump (Masterflex model 77601-60, Premier Pump), 5L stainless steel tank (Eagle Stainless), and Pt-cured silicone rubber tubing (Saint-Gobain 3355L). The feed tank was heated by a hot plate, with a magnetic stir-bar for mixing. The stainless steel feed tank was cleaned and the silicone tubing replaced when carryover or back extraction of broth components into subsequent runs was a concern. A schematic is shown in Fig. 3.

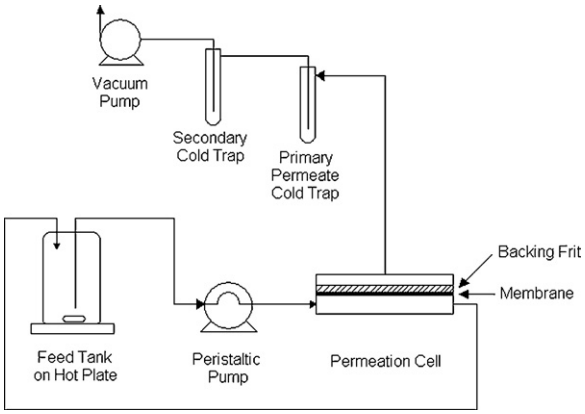

Fig. 3. Schematic of the "Impurities" rig and "Conditioning" rig.

The conditioning rig was similar to the impurities rig. It used the same permeation cell design and vacuum pump as above, but the feed system consisted of a peristaltic pump (Masterflex L/S, Cole Parmer) and a 250 ml glass bottle as a feed vessel placed in a water-filled dish heated by a hot plate. Tubing was stainless steel, except at the pump head where 1/8" ID silicone tubing was used. The stainless steel tubing was cleaned and the silicone tubing replaced after every use to avoid carryover or back extraction of broth components into subsequent runs. A cold trap protected the vacuum pump from permeate contamination.

2.4. Feed components and solutions

Corn fermentation broth was obtained from the beer well (holding tank between fermenters and first distillation column) of a dry-grind corn fuel ethanol plant (Cilion, Inc., Keyes, CA). Madson and Monceaux [19] provide details of the dry-grind fuel ethanol production process. The broth containers were cooled on ice and partially degassed, then frozen. When needed, a portion of the broth was thawed, centrifuged to remove solids at 4 °C for 10 m, the supernatant decanted and recentrifuged at 4 °C for 60 min, then filtered through coarse filter paper to remove the low density solids. The filtrate was slightly cloudy. It was sampled and analyzed for ethanol content, and refrigerated until used. Because some ethanol was lost during processing, the concentration was adjusted to the desired value with 100% ethanol when the broth was charged to the pervaporation rig.

In a dry-grind corn fuel ethanol plant, the bottoms from the first distillation column are centrifuged; thin stillage is the supernatant. Thin stillage was collected by USDA's Eastern Regional Research Center (ERRC) at Wyndmoor, PA. from the Western New York Energy plant (Medina, NY). The thin stillage sample was stored frozen. It contained significant amounts of solids. An oil film was seen on the surface of the thin stillage. When needed, a portion of thin stillage was thawed and processed in the same way as the Cilion fermentation broth. The liquid fraction of the thin stillage was characterized by HPLC at ERRC. The concentration of selected components was 0.04% ethanol, 1.54% glycerol, 0.15% succinic acid, 1.12% methanol, 0.09% acetic acid, 0.11% lactic acid, 0.06% glucose, 1.2% maltose, maltotriose and higher soluble dextrins.

A synthetic fermentation broth based on a syngas feed was prepared. The medium was based on the recipe in US Patent Application 20080305539 [20]. Instead of using the patent application's active culture of *Clostridium ragsdalei* and a syngas feed mixture to produce ethanol, a simulated product broth was made by adding to the medium 0.5 g/L yeast extract, 30 g/L ethanol, 0.2 g/L protein (albumin, bovine fraction V), and 4.38 g/L *Lactobacillus acidophilus*.

Other chemicals used to make feed solutions were succinic acid (Sigma–Aldrich, 99+%), glycerol (Aldrich, 99.5+%), corn oil (Safeway, 100%), oleic acid (Sigma–Aldrich, 99%), and glycine (Research Organics, "Ultra Pure"), and ethanol (Pharmco-Aaper, absolute, anhydrous). Water used to prepare feed solutions was treated by ion exchange and reverse osmosis, then further purified to Type I water with a resistivity of 17 MΩ-cm (Barnstead NANOpure system).

2.5. Analytical method

Permeate was poured out of the trap into a vial, and the trap rinsed twice with 4–5 ml flushes of anhydrous benzyl alcohol. The rinses were added to the vial containing the permeate. If two phases resulted, additional benzyl alcohol was added. Note that ethanol is

miscible with benzyl alcohol, but water has a solubility of about 10% at room temperature. The internal standard solution (5 wt% 1-hexanol in anhydrous benzyl alcohol) was weighed into the vial, and the solution was analyzed for both ethanol and water by gas chromatography with an HP 6890 GC with a thermal conductivity detector using a DBWax-etr 30 m capillary column. The calculated mass of ethanol and of water in the permeate by the GC analysis was compared with the weight of permeate in the trap as calculated from the gross and tare weight of the trap. Agreement was usually within 2%. The feed solution was analyzed similarly, but if solids were present, the solution was prefiltered (Pall Acrodisc 0.2 μm Supor membrane syringe filter).

2.6. Data treatment

Total flux J (g/m^2 h) was calculated as

$$J = \frac{W}{At} \quad (1)$$

where W is the mass (g) of permeate collected, A is the area (m^2) of the membrane exposed to the feed, and t is the time (h) that permeate was collected in the trap. The process separation factor β (dimensionless) was

$$\beta = \frac{[E]_p/[E]_f}{[W]_p/[W]_f} \quad (2)$$

where $[E]_p$ is the ethanol concentration in the permeate (wt%), $[E]_f$ is the ethanol concentration in the feed, $[W]_p$ is the water concentration in the permeate, and $[W]_f$ is the water concentration in the feed.

The thickness of the membranes used here varied from 159 to 318 μm, average feed concentration varied as much as 10% over several days of operation, and temperature varied up to 2° from the 50 °C desired temperature. Therefore, the flux data have been normalized to a standard membrane thickness of 100 μm and a standard driving force based on feed temperature of 50.0 °C, permeate pressure of 0 torr, and the desired feed concentration (5.0 wt% for most runs, 12.0 wt% for the corn fermentation broth, 3.0 wt% for the syngas fermentation broth). This was done by calculating permeability coefficients for each run using an equation derived from the solution–diffusion model [21]:

$$J_i = \frac{P^G_i}{l}\left(\gamma^L_{i0} x^L_{i0} p^{sat}_{i0} - p_{il}\right) \quad (3)$$

where for component i, J_i is the partial flux, $P^G{}_i$ is the permeability coefficient, l is the membrane thickness, $\gamma^L{}_{i0}$ is the activity coefficient in the feed liquid, $x^L{}_{i0}$ is the mole fraction in the feed liquid, $p^{sat}{}_{i0}$ is the pure component vapor pressure, and p_{il} is the partial pressure in the permeate vapor. The permeability coefficients calculated from actual operating conditions and membrane thickness were then used to recalculate the partial fluxes at the standard conditions. The driving force (and thickness) normalized total flux (N.F.) is the sum of the two partial fluxes. The pure component vapor pressures come from the Antoine equation using parameters from Gmehling and Onken [22]. Activity coefficients for ethanol–water solutions are from Gmehling et al. [23]. While this calculation is accurate for clean binary feeds, when salts and other components are present the ethanol and water activity coefficients will be affected. However, errors in calculating the driving force-normalized flux for the broths and spiked feeds using the binary activity coefficients should be minor since the permeability coefficients are also derived using the assumption of binary ethanol–water systems, and the reverse application to adjust the partial fluxes should largely offset deviations from the true activity coefficients.

3. Results and discussion

3.1. Spiking studies

Spiking tests with succinic acid and glycerol were each run in the impurities rig. Fig. 4 shows the sequence of operations and the performance results for the succinic acid test. A three-day baseline for the 60 wt% ZSM-5/PDMS membrane on clean 5 wt% ethanol was generated, then succinic acid was added to the feed tank to generate a 0.15 wt% solution, and operation continued. This concentration was chosen as being representative of that found in a fermentation broth (confirmed by analysis of thin stillage; see Section 2.4). The pH of the solution was 3.2. For succinic acid the pK_1 is 4.21, and pK_2 is 5.64, hence this acid is largely in the protonated form at this pH, and might be expected to partition in PDMS more than the ionized form. The membrane was operated 6 days on this solution, with virtually no change in the separation factor, but a slow reduction in normalized flux. When the pH of the feed solution was then adjusted to 7.0 with sodium hydroxide, the separation factor began to decline slightly, and the flux slowed its rate of decline. This was unexpected, as succinic acid should have been less able to partition into the membrane at the higher pH.

Fig. 5 shows the sequence of operations and the performance results for the glycerol test. In this particular test, the MMM had a higher zeolite loading of 73 wt%, compared to the standard 60 wt% used in all other tests, which resulted in an initially higher separation factor and normalized flux than the other membranes. Again, a three-day baseline on clean 5 wt% ethanol was done, then glycerol was added to the feed tank to make a 1 wt% solution, and operation continued for another 6 days. A slight reduction in separation factor occurred during the baseline period and continued at the same rate after glycerol addition to the feed. Normalized flux also decreased during the baseline period and the first two days after glycerol addition, then stabilized for the subsequent four days.

The synthetic feeds containing either succinic acid or glycerol showed some performance decline in ethanol separation and flux for the MMMs, but neither of these tests produced the dramatic performance decline that was anticipated based on prior literature.

3.2. Fermentation broth–corn feedstock

The sequence of operations of the impurities rig, and the performance of a 60 wt% ZSM-5/PDMS mixed matrix membrane with the centrifuged and coarse-filtered corn fermentation broth is shown

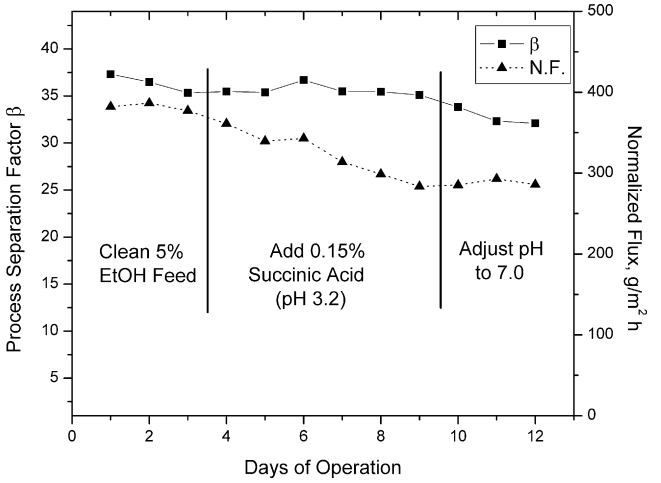

Fig. 4. Ethanol–water separation factor and driving-force normalized flux vs. time for pervaporation with a 60 wt% ZSM-5/PDMS membrane on clean feed and feed spiked with 0.15 wt% succinic acid.

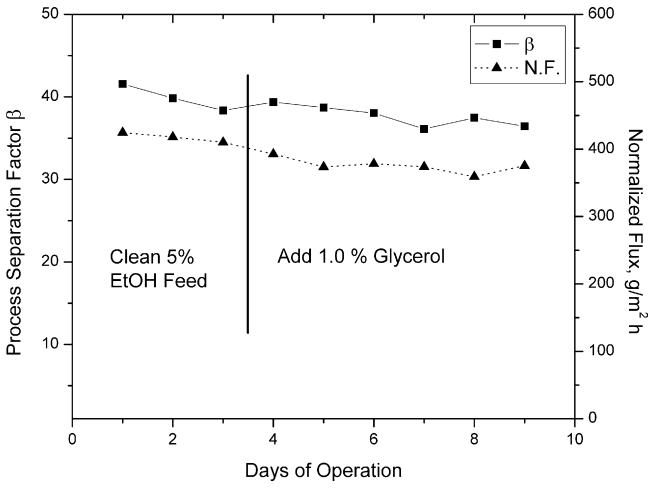

Fig. 5. Ethanol–water separation factor and driving-force normalized flux vs. time for pervaporation with a 73 wt% ZSM-5/PDMS membrane on clean feed and feed spiked with 1 wt% glycerol.

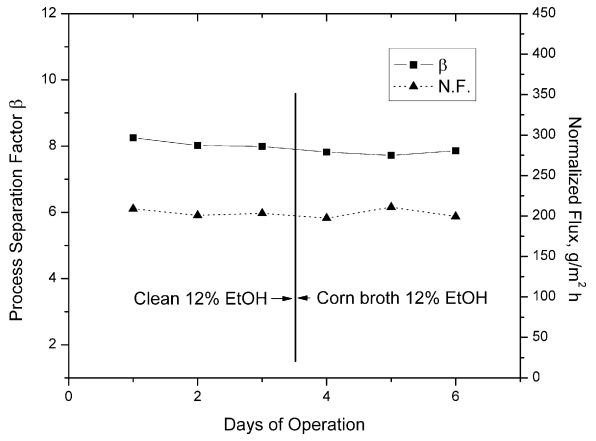

Fig. 7. Ethanol–water separation factor and driving-force normalized flux vs. time for pervaporation with a PDMS membrane on clean feed and dry-grind corn fermentation broth.

in Fig. 6. The membrane was first run in the clean feed rig for 4 days using clean 5 wt% ethanol feed. Results showed typical performance stability. Then the cell with the membrane was transferred to the impurities rig where it was run for an additional 7 days on clean 5 wt% ethanol feed. Flux was reasonably steady, but separation factor dropped a small but consistent amount each day. Next, to duplicate the concentration of ethanol in the corn fermentation broth, the feed solution was changed to a clean 12 wt% ethanol solution and run for 3 days. This resulted in an expected increase in the normalized flux. This solution was drained and the corn fermentation broth charged. It was run for 7 days at its native pH of 3.4. After the first day of operation on the broth, performance was drastically reduced. Separation factor dropped from 25.8 to 13.6 and normalized flux from 317 to 113 g/m^2 h. These reduced values stayed relatively constant for the 7 days. On the theory that carboxylic acids may be contributing to the performance reduction the pH was adjusted to 7.0 with sodium hydroxide and the membrane was run 2 more days to attempt to back-extract the acids from the membrane. With a pK of about 4, carboxylic acids adsorbed in the membrane may be induced to partition into the feed where they would be converted to the ionized form, with a higher water solubility and a lower polymer solubility. However, 2 days of operation at pH 7 did not improve the performance. Next, an attempt was made to improve the membrane's performance by flushing and running on a clean ethanol/water solution. The system was drained and the membrane, cell and system were flushed repeatedly with water, drained, charged with 12 wt% ethanol, pervaporated one day, drained, and recharged with clean 12 wt% ethanol. Over 3 days of subsequent operation, the flux remained steady and low at 113 g/m^2 h, and, instead of improving, the separation factor continued to decrease to about 10.

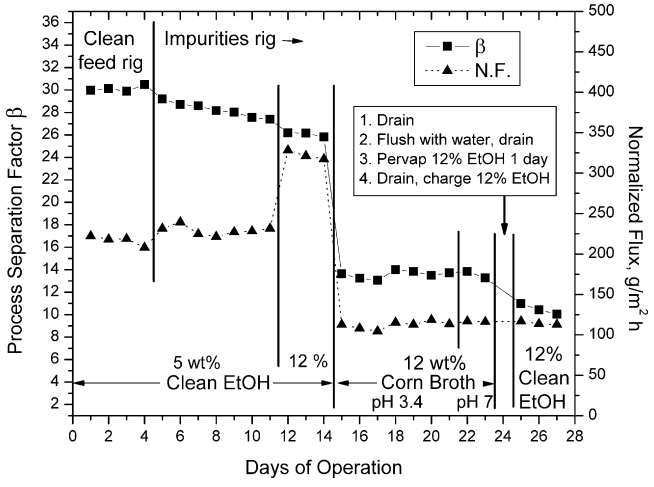

Fig. 6. Ethanol–water separation factor and driving-force normalized flux vs. time for pervaporation with a 60 wt% ZSM-5/PDMS membrane on clean feed and dry-grind corn fermentation broth.

Degradation of MMM performance by the broth was significant and rapid, and was not improved by flushing or operation on clean ethanol/water solutions.

Another test was run using a homogeneous PDMS membrane (no zeolite filler), as shown in Fig. 7. Initially the PDMS membrane was run on clean 12 wt% ethanol, with typical results of normalized flux of 204 g/m^2 h and separation factor of 8.1. The feed was then changed to the corn fermentation broth and operation continued for another 3 days. Normalized flux averaged 203 g/m^2 h and the separation factor averaged 7.8 during pervaporation of the broth.

This test suggested that fouling of the membrane surface was not significant, and that the zeolite particles in the MMM were being strongly affected by broth components. In fact, the MMM separation factor was declining to near that of the pure PDMS membrane, and MMM normalized flux was lower than for the PDMS membrane, indicating near-total conversion of the ZSM-5 particles to inactive filler. As others have proposed, a competitive adsorption mechanism is plausible wherein molecules are more strongly adsorbed than ethanol in the zeolite, and desorption becomes problematic at the temperature employed. Long et al. [24] used TGA to study desorption temperatures for a range of molecules from silicalite-1. While the desorption peak for ethanol occurred at 75 °C, 1-propanol was at 110, acetic acid at 128, and 1-pentanol at 141 °C, for example. This lends strength to the theory that the zeolite pores are being blocked to ethanol by more strongly-adsorbing species.

3.3. Fermentation broth–syngas feedstock

Runs were carried out in the impurities rig by directly pervaporating the syngas synthetic fermentation broth continuously for several days. Fig. 8 shows the sequence of operations of the impurities rig, and the performance of a 60 wt% ZSM-5/PDMS mixed matrix membrane. The membrane was first run in the clean feed rig for 3 days using clean 5 wt% ethanol feed. Then the cell with the membrane was transferred to the impurities rig where it was run for 3 days on clean 3 wt% ethanol feed, to duplicate the ethanol concentration in the syngas fermentation broth. Flux was steady,

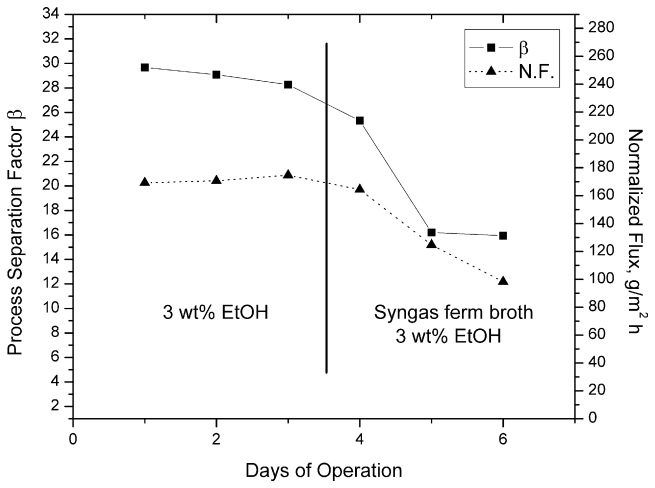

Fig. 8. Ethanol–water separation factor and driving-force normalized flux vs. time for pervaporation with a 60 wt% ZSM-5/PDMS membrane on clean feed and synthetic syngas fermentation broth.

but separation factor dropped a small but consistent amount each day. This solution was drained and the syngas fermentation broth described in Section 2.5 was charged. It was run for 3 days. After the first day of operation on the broth, performance was reduced, and continued to decline thereafter. With the clean 3% ethanol feed, separation factor was 28.3 and normalized flux was 175 g/m^2 h. At the end of the 3 days of pervaporation of the synthetic syngas fermentation broth, separation factor fell to 15.9 and normalized flux to 98 g/m^2 h.

3.4. Conditioning method and results

Several of the feed solutions to be tested were in short supply, and were being rapidly consumed by the large volume requirement for the impurities rig. Also, back-extraction into subsequent runs was occurring for broth components absorbed into the silicone rubber tubing used in the impurities rig feed system. This necessitated frequent replacement of the tubing, which was expensive. An alternate test method was developed to reduce the amount of feed solution used in each run, and avoid the need to frequently replace the tubing. Since the performance degradation with the corn fermentation broth was not reversible by flushing and changing the feed to a clean ethanol/water solution, it was theorized that exposure of a MMM to the broth, perhaps by simply soaking it in the broth, would result in a significant poisoning of the ZSM-5, which could then be measured using a clean ethanol/water feed in the impurities rig.

It was found that simple soaking of the MMM in the corn fermentation broth did not dramatically reduce its performance. Soaking conditions of (1) 18 h at room temperature, (2) 22 h at 50 °C, (3) 18 h at 50 °C in a permeation cell with vacuum applied to the permeate side (the feed side was stagnant), and (4) 25 h at 72 °C in a permeation cell with vacuum applied to the permeate side (the feed side was stagnant), all failed to reproduce the dramatic performance reductions seen in the impurities rig. However, operation in the conditioning rig under pervaporation conditions with a slowly flowing feed was effective in reproducing the seriously degradation of performance seen in the impurities rig.

Three baseline (pre-conditioning) days of operation were carried out in the clean feed rig on a clean 5 wt% ethanol feed and the separation factor and normalized flux data averaged. The membrane was conditioned for 8 h at 50 °C in the conditioning rig. Then the membrane was evaluated for 3 days in the impurities rig on a clean 5 wt% ethanol feed and the separation factor and normalized flux data averaged. Table 1 shows the mean and standard deviation pre- and post-conditioning, and the ratio of the post- to the pre-mean values for the process separation factor and the driving force-normalized flux for each conditioning solution tested.

Conditioning with the corn fermentation broth emulated the dramatic drop in performance shown in Fig. 6 for impurity rig operation on the broth.

Corn oil is a known component of corn fermentation broth. A corn oil emulsion conditioning solution of 9% corn oil and 44% ethanol in water was prepared. This ratio of components was chosen to generate a stable emulsion by balancing the densities of the phases. This conditioning immediately and drastically reduced MMM performance. Triglycerides comprise the bulk of corn oil, but it is unlikely they were creating this effect as these triglycerides are too large to enter the 5.5 Å diameter ZSM-5 pores. However, corn oil also contains some free fatty acids, which do not have this limi-

Table 1
Performance of 60 wt% ZSM-5/PDMS and PDMS membranes pre- and post-conditioning.

Conditioning solution	MMM zeolite content, wt%	Process separation factor β			Driving force-normalized flux, g/m^2 h		
		$\frac{\beta\,\text{post}}{\beta\,\text{pre}}$	β pre, mean (s.d.)	β post, mean (s.d.)	$\frac{\text{N.F. post}}{\text{N.F. pre}}$	N.F.pre, mean (s.d.)	N.F.post, mean (s.d.)
Corn fermentation broth, centrifuged, coarse-filtered	59.7	0.55	29.6(1.0)	16.2(0.6)	0.57	194(7)	111(4)
Corn oil emulsion (9% corn oil, 44% ethanol)	60.1	0.27	21.4(0.4)	5.8(0.2)	0.43	254(4)	110(6)
Oleic acid emulsion (8% oleic acid, 50% ethanol)	60.0	0.22	20.5(0.4)	4.5(0.3)	0.30	253(3)	76(11)
Corn oil emulsion (9% corn oil, 44% ethanol)	0	0.99	9.3(0.14)	9.3(0.03)	0.96	91(2)	87(0.6)
Clean 50% ethanol	60.2	0.94	33.5(1.1)	31.4(0.4)	1.04	203(1)	210(1)
Corn fermentation broth, centrifuged, coarse-filtered, extracted with isooctane	60.0	1.13	22.0(0.7)	24.8(1.4)	0.88	235(3)	207(7)
Thin stillage: most of oil removed (centrifuged, coarse-filtered, fortified to 8.6% ethanol)	60.0	0.90	23.0(0.5)	20.7(0.8)	0.84	285(19)	240(9)
Thin stillage: oil re-added (centrifuged, coarse-filtered, oil in centrifuge tubes removed with 95% ethanol and re-added (50% thin stillage, 45% ethanol))	60.2	0.38	20.0(0.2)	7.6(1.9)	0.31	259(2)	81(19)
Succinic acid (1% succinic acid, 5% ethanol)	60.1	0.89	31.4(0.5)	28.0(0.4)	0.83	221(1)	183(1)
Glycerol (1% glycerol, 5% ethanol)	60.0	1.00	30.8(0.4)	30.8(0.5)	0.78	214(32)	168(4)
Glycine (1% glycine, 5% ethanol)	60.2	0.92	25.4(0.4)	23.3(1.2)	1.06	224(1)	236(3)
Syngas base solution (with minerals, trace metals, vitamins solutions, pH adjustment, reducing agent solution, yeast extract, 3.4% ethanol. No added protein or cells)	59.9	0.96	31.8(3.2)	30.5(0.7)	1.12	194(3)	217(4)

tation. An oleic acid emulsion conditioning solution of 8% oleic acid and 50% ethanol was prepared. This had the most detrimental effect on the MMM of any solution tested.

A conditioning run was made with the corn oil emulsion on a PDMS membrane. Separation factor and normalized flux were essentially unchanged, implying that the dramatic effect is associated with the zeolite.

A conditioning run was made with clean 50% ethanol to determine whether the high level of ethanol used in the emulsion runs was affecting MMM performance. Separation factor decreased very slightly, and flux increased very slightly.

The corn fermentation broth was extracted with isooctane and the aqueous phase used in a conditioning run. Isooctane was chosen as the extraction solvent because the molecule is too large to enter the 5.5 Å diameter pores of the zeolite. The broth was mixed in a separatory funnel with isooctane in a weight ratio of broth:solvent of 4:1 and then allowed to phase-separate. The upper solvent phase was an emulsion that separated very slowly into a clear yellow isooctane layer and an emulsion layer after 4 days. The lower aqueous phase was drained off and represented a 94% recovery of the original broth charge. The aqueous phase was adjusted to 8.5 wt% ethanol and a MMM was conditioned. A small step-change in performance occurred with separation factor increasing 13% and normalized flux decreasing 12%. The treatment was very effective in eliminating the dramatic reduction in performance.

The centrifuged and coarse-filtered thin stillage was run in the conditioning rig, resulting in about 10% decrease in performance, but did not show a strong effect on the membrane tested. However, it was observed that an oil layer was separating out on the surface of the centrifuge tubes, and more was being removed by the coarse filtration. A second thin stillage conditioning solution was prepared wherein the oil in the centrifuge tubes was washed out with 95% ethanol and returned to the filtered thin stillage solution. This resulted in a composition of about 50% thin stillage and 45% ethanol, plus the recovered corn oil. This solution had an immediate and deleterious effect on the MMM.

Conditioning solutions of 1% succinic acid in 5% ethanol, and 1% glycerol in 5% ethanol were run. The succinic acid level was nearly 7 times higher than the spiking study run done in the impurities rig as described in Section 3.1. For succinic acid, separation factor dropped 11% and flux 17%. Glycerin had no effect on separation factor, and while the ratio of the post- to pre-conditioning flux was reduced, variability of the flux data was high.

To explore the effect of an amino acid, a run was carried out on 1% glycine in 5% ethanol. Again, there was a small step-change in performance but no dramatic effect, with separation factor dropping slightly and flux increasing slightly.

Finally, a conditioning solution of the synthetic syngas fermentation base stock solution was prepared. This comprised the minerals, trace metals, and vitamins solutions, the pH adjustment, the reducing agent solution and the yeast extract, but the protein and the cells were not added. This was fortified to 3.4% ethanol. Separation factor dropped slightly, and normalized flux immediately increased slightly. This suggests that cells, cell components and/or protein present in the full broth tested in Section 3.3 but missing from this conditioning test may be responsible for the performance decrease seen in the study with the full broth.

3.5. Broth pretreatment discussion

For the system and membranes used here, a very rough estimate of the amount of zeolite present in a thick membrane, and the concentration in the feed solution of a "poison" that would inactivate this amount of zeolite indicated that very low concentrations of a poison in the feed would be sufficient. The zeolite has a surface area of 400 m^2/g. To estimate the mass of a poison that would totally occlude this surface area, a series of assumptions are made. Choose a sorbent occluded area of 30 $Å^2$ per molecule sorbate, assume that adsorption is irreversible, and further that all the sorbate in the feed is transferred over time to the sorbent. Then a sorbate monolayer that totally occluded the zeolite's surface would contain 2.2×10^{-3} gmol sorbate per gram of zeolite. If the sorbate's molecular weight were 300, then the ratio of poison to zeolite would be 0.66 to totally occlude the surface area of the zeolite. A typical membrane is 60 wt% zeolite, 250 μm thick, with an exposed surface area of 16.13 cm^2 and a membrane density of ca. 1.27 g/cm^3. This volume of membrane would contain ca. 0.3 g zeolite, which would be poisoned by adsorption of 0.2 g poison. This amount of poison in 4 L of feed solution yields a concentration of 0.005 wt%, or 50 ppm. There are many assumptions inherent in this calculation, but the intent is to derive an order-of-magnitude estimate.

In a commercial environment, an ethanol-selective mixed matrix membrane will be a thin-film composite in order to achieve economical flux. Since the zeolite content per m^2 will be one to two orders of magnitude lower for a TFC compared to the thick, unsupported membranes studied here, membrane performance reduction under similar circumstances will be that much more rapid. Consider a typical fuel ethanol plant with a capacity of 50 million gal/year of anhydrous ethanol. Assume a membrane ethanol flux of 1 kg/m^2 h. The membrane area required is 17,760 m^2. If membrane and equipment cost is taken as \$200/m^2, the investment would be \$3.6 million. Assume an active layer MMM thickness of 15 μm and a 60 wt% zeolite loading. The amount of zeolite present in the membrane would be 200 kg. Using the sorbate calculation above, this 200 kg of zeolite would be poisoned by 132 kg of this impurity. If the impurity were present at 50 ppm in a 5 wt% ethanol feed, the membrane would be poisoned in less than 8 h. Regeneration of the membrane, for instance by heating to desorb the low volatility components, does not seem practical as more time would be spent in regeneration than in operation of the membrane. Again, this is a very simplistic calculation, but it indicates the severity of the problem.

The implications are that (1) the membrane is expensive and to have a useful lifetime, must be protected from poisons, (2) pretreatment of the feed to remove the poisons is required, (3) the pretreatment method(s) must be extremely efficient and reliable, and (4) the pretreatment method(s) must be inexpensive, because fuel ethanol is a high volume, low value product and margins will be low. These are significant challenges.

There are a variety of fermentation broth pretreatment options which may have some degree of effectiveness in protecting a ZSM-5/PDMS mixed matrix membrane from rapid performance degradation. Adsorption, extraction (as demonstrated in Section 3.4), flocculation, flotation, ultrafiltration and vaporization are potential feed pretreatment options. A process based on vaporization, for instance, might comprise partial vaporization of the fermentation broth, producing a vapor enriched in ethanol and lacking the higher boiling components such as the fatty acids, glycerol, etc. An ethanol-selective vapor permeation membrane system could then enrich this stream to a concentration where water-selective membrane permeation could purify the ethanol to fuel-grade. Heat recovery from condensing the retentate vapor from the ethanol-selective membrane would reduce the heat load in the initial vaporization step. Following this or another of these methods, a "polishing" treatment comprising a guard bed of ZSM-5 to adsorb any traces of remaining poisons would be advisable.

Other options include the use of an adsorbent in the MMM that is not poisoned by more strongly adsorbing impurities, or use of some sort of protective layer between the MMM active layer and the feed solution that was impermeable to these poisons but did

not significantly reduce membrane flux or selectivity. These are all areas that deserve future evaluation.

4. Conclusions

Mixed matrix membranes of ZSM-5 in PDMS at 60wt% loadings and above were successfully prepared. Pervaporation of ethanol was carried out using clean feeds to establish baseline performance, and then using clean feeds spiked with selected components or fermentation broths with various treatments. In addition, conditioning of membranes via pervaporation of a test solution followed by performance testing on clean ethanol solution proved effective in identifying impurities and solutions that drastically degraded membrane performance. Performance reduction of the ZSM-5/PDMS membranes was rapid and significant for contact with the fermentations broths, but no performance reduction was seen with pure PDMS membranes, indicating that the zeolite component is being inactivated. Inactivation could be greatly reduced for the corn fermentation broth or thin stillage by removal of the corn oil fraction (and probably other components more hydrophobic than ethanol) by solvent extraction or adsorption/absorption. Oleic acid, as a representative fatty acid present in corn oil, was extremely detrimental to the membranes. There are a variety of potential pretreatment options, but the challenge will be significant to reduce poisons to a negligible level at a low cost.

Conflict of interest

There is no conflict of interest.

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